

Durham Research Online

Deposited in DRO:

23 May 2017

Version of attached file:

Accepted Version

Peer-review status of attached file:

Peer-reviewed

Citation for published item:

Crassous, J. and Hellou, N. and Srebro-Hooper, M. and Favereau, L. and Zinna, F. and Caytan, E. and Toupet, L. and Dorcet, V. and Jean, M. and Vanthuyne, N. and Williams, J. A. G. and Di Bari, L. and Autschbach, J. (2017) 'Enantiopure cycloiridiated complexes bearing a pentahelicenic N-heterocyclic carbene and displaying long-lived circularly-polarized phosphorescence.', *Angewandte chemie international edition.*, 56 (28). pp. 8236-8239.

Further information on publisher's website:

<https://doi.org/10.1002/anie.201704263>

Publisher's copyright statement:

This is the peer reviewed version of the following article: Crassous, J., Hellou, N., Srebro-Hooper, M., Favereau, L., Zinna, F., Caytan, E., Toupet, L., Dorcet, V., Jean, M., Vanthuyne, N., Williams, J. A. G., Di Bari, L. Autschbach, J. (2017). Enantiopure cycloiridiated complexes bearing a pentahelicenic N-heterocyclic carbene and displaying long-lived circularly-polarized phosphorescence. *Angewandte Chemie International Edition* 56 (28): 8236-8239, which has been published in final form at <https://doi.org/10.1002/anie.201704263>. This article may be used for non-commercial purposes in accordance With Wiley-VCH Terms and Conditions for self-archiving.

Additional information:

Use policy

The full-text may be used and/or reproduced, and given to third parties in any format or medium, without prior permission or charge, for personal research or study, educational, or not-for-profit purposes provided that:

- a full bibliographic reference is made to the original source
- a [link](#) is made to the metadata record in DRO
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the [full DRO policy](#) for further details.

Enantiopure cycloiridiated complexes bearing a pentahelicenic N-heterocyclic carbene and displaying long-lived circularly-polarized phosphorescence

Nora Hellou,^[a] Monika Srebro-Hooper,^{*[b]} Ludovic Favereau,^[a] Francesco Zinna,^[c,d] Elsa Caytan,^[a] Loïc Toupet,^[a] Vincent Dorcet,^[a] Marion Jean,^[e] Nicolas Vanthuyne,^[e] J. A. Gareth Williams,^[f] Lorenzo Di Bari,^[c] Jochen Autschbach,^[g] and Jeanne Crassous^{*[a]}

Abstract: A fused π -helical N-heterocyclic (NHC) system was prepared and examined through its diastereoisomerically pure cycloiridiated complexes. The latter display light-green phosphorescence with unusually long lifetimes and circular polarization that depends on both the helical-NHC *P/M* and the iridium Δ/Λ stereochemistry. These unprecedented features are attributed to extended π -conjugation within helical carbenic ligand and efficient helicene-NHC-Ir interaction.

Octahedral cyclometalated iridium(III) complexes^[1] have attracted attention due to their applications as phosphors in organic light-emitting devices (OLEDs),^[2] and for their biological activity.^[3] To date, several classes of enantiopure cycloiridiated systems have been reported.^[1b,4] As for Ir(III) complexes bearing N-heterocyclic carbene (NHC) ligands, while few examples have been shown to display deep blue phosphorescence (a challenging target in the OLED area^[5,6]), *chiral* NHC-based systems for molecular materials science are almost unknown. Furthermore, no chiral purely π -helical NHC has been reported to date.^[7,8] Herein, we describe the synthesis of a π -conjugated *ortho*-fused [5]helicenic NHC ligand (in which an NHC is incorporated within a helical core) through its diastereoisomerically pure cycloiridiated complexes **A**^{1,2} (Figure 1). We detail their electronic and structural features, stereochemistry, photophysical and chiroptical properties experimentally and computationally.

Scheme 1 shows the strategy to prepare the [5]helicene-imidazolium iodide salt (\pm)-**5**. First, the [5]helicene-thiadiazole **1**^[9a] was reduced to 1,2-diamino-[4]helicene **2** with LiAlH₄,^[9b] which was then directly cyclized to the precarbenic [5]helical imidazole **3** using triethyl orthoformate in the presence of catalytic iodine in acetonitrile.^[9c] To our knowledge **3** is the first fully π -*helicenic* imidazole since it displays five *ortho*-fused aromatic rings including the terminal imidazole cycle.

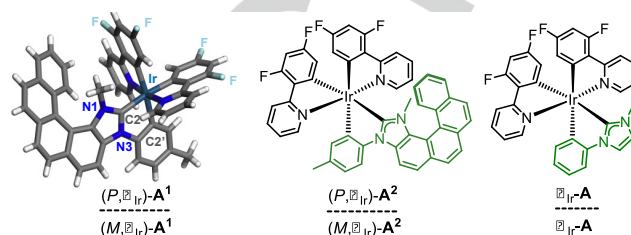
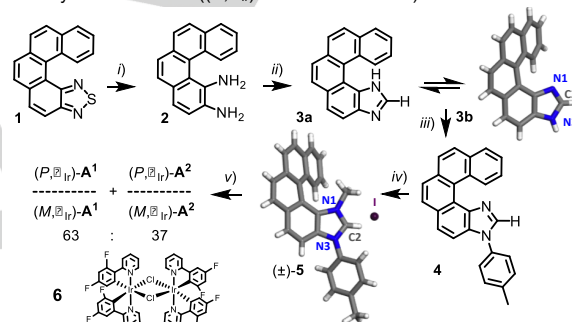


Figure 1. Meridional cycloiridiated complexes **A**^{1,2} bearing a *P*-[5]helicene-NHC chelating ligand (in grey) and model NHC complex **A** lacking the helicene unit.^[5c] X-ray structure of **A**¹ ((*P*, Δ)_{Ir} enantiomer shown).



Scheme 1. Preparation of [5]helicene-imidazolium salt (\pm)-**5** and of cycloiridiated complexes **A**^{1,2}. i) LiAlH₄, THF, Ar, r.t., 5 hrs; ii) HC(OEt)₃, cat. I₂, CH₃CN, r.t. 2 hrs, 52% (two steps); iii) *p*-tolyl-boronic acid, anhydrous Cu(OAc)₂, pyridine, CH₂Cl₂, air, molecular sieves, r.t., 24 hrs, 69%; iv) CH₃I, CH₃CN, reflux, 18 hrs, 91%; v) **6**, Ag₂O (2 eq.), 1,2-dichloroethane, 90°C, 16 hrs, dark, 76%. X-ray structures of tautomer (\pm)-**3b** and of (\pm)-**5** (*P* enantiomers shown).

Two tautomeric forms^[10a] (**3a,b** in Scheme 1) are seen by ¹H NMR spectroscopy (Figure S2 in SI) and are in exchange at 75°C on the NMR timescale. X-ray crystallography ascertained the helical nature of **3**, which crystallized as its **3b** tautomer in the *Ia* centro-symmetric space group, with both *P* and *M* enantiomers (Scheme 1, SI). The imidazole ring reveals classical metric data (C2–N1 (C2–N3) bond-length: 1.320 (1.345) Å,^[10b] while the molecule shows a helicity (dihedral angle between the terminal rings) of 42.27°. A Chan-Lam coupling^[11] of **3** with *p*-tolyl-boronic acid furnished **4**, whose methylation with CH₃I in excess gave the imidazolium salt (\pm)-**5**. While the [5]helicenic imidazole derivatives **3** and **4** are configurationally unstable in solution (the enantiomers could not be resolved by chiral HPLC at 10°C, which indicates an inversion barrier <90 kJ mol^{−1}), the methyl group in the inner 1 position of **5** blocks the inversion of the helix (*vide infra*).[‡] (\pm)-**5** crystallized in the *P2*₁/*n* centro-symmetric space group, with heterochiral dimers of *P* and *M* enantiomers, and displays a helicity higher than **3** (50.81°), while the *p*-tolyl group forms a dihedral angle of 43.67° with the imidazolium cycle (Scheme 1, SI). **5** can be regarded as a 1*N*-Me-[5]helicene derivative.^[12]

- [a] Dr. N. Hellou, Dr. L. Favereau, Dr. E. Caytan, Dr. V. Dorcet, Dr. L. Toupet, Dr. J. Crassous, Institut des Sciences Chimiques de Rennes UMR 6226, Institut de Physique de Rennes, UMR 6251, CNRS Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex (France). E-mail: jeanne.crassous@univ-rennes1.fr
- [b] Dr. M. Srebro-Hooper, Faculty of Chemistry, Jagiellonian University, 30-060 Krakow (Poland). Email: srebro@chemia.uj.edu.pl
- [c] Dr. F. Zinna, Prof. L. Di Bari, Dipartimento di Chimica e Chimica Industriale (University of Pisa), via Moruzzi 13, 56124, Pisa (Italy).
- [d] Present address: Université de Genève, Département de Chimie Organique, Quai Ernest-Ansermet 30, 1211 Genève 4 (Switzerland).
- [e] M. Jean, Dr. N. Vanthuyne, Aix Marseille University, CNRS, Centrale Marseille, iSm2, Marseille (France).
- [f] Prof. J. A. G. Williams, Department of Chemistry, University of Durham, Durham, DH1 3LE (UK).
- [g] Prof. J. Autschbach, Department of Chemistry, University at Buffalo, State University of New York, Buffalo, NY 14260 (USA).

Supporting information for this article is given via a link at the end of the document. (Please delete this text if not appropriate)

The heteroleptic cycloiridiated complexes **A**^{1,2}, bearing a [5]helicene-NHC-*N*-tolyl and two 2-(2,4-difluorophenyl)-pyridyl (dfppy) ligands, were obtained by reacting **5** with Ag₂O and [Ir(μ-Cl)(dfppy)₂]₂ **6** (Scheme 1, SI).^[5,13] The diastereoisomeric mixture of **A**¹ and **A**² was obtained in the respective 63:37 ratio, as estimated via ¹H NMR spectroscopy and HPLC (SI), suggesting that the cyclometalation is diastereoselective. **A**^{1,2} correspond to the meridional geometric isomers, indicating that the mutually *trans* disposition of the pyridyl rings of the precursor **6** is retained,^[5,13] as further evidenced by ¹H-¹H NOESY and ¹H-¹⁹F HOESY NMR studies (SI). X-ray crystallography of the pure diastereoisomer **A**¹ (*I*₄/*a* centro-symmetric space group, Figure 1, SI) shows the pseudo-octahedral geometry around the iridium center and the *trans* relationship of the pyridyl rings of the two dfppy ligands, whereas the [5]helicene-NHC chelate orientates in two ways around the Ir(III), defining either the Δ_{Ir} or Λ_{Ir} epimers associated respectively with the *M* or *P* helical stereochemistry ((*M*,Δ_{Ir})- and (*P*,Δ_{Ir})-**A**¹) [the other diastereoisomers are (*P*,Δ_{Ir})- and (*M*,Δ_{Ir})-**A**²]. It depicts also the chiral, purely helical, N-heterocyclic carbenic ligand, with its five *ortho*-fused rings and the NHC cycle bound to the Ir with C2–Ir bond-length of 2.051 Å, and C2–N1 (C2–N3) of 1.368 (1.366) Å.^[14] Furthermore, the C2' of the tolyl group is coordinated to the metal (C2'–Ir: 2.102 Å) and is almost coplanar with the NHC cycle (dihedral angle: 3.92°). These metric data correspond to classical values for carbenic cycloiridiated complexes.^[5c-e] The ¹³C NMR spectra of **A**^{1,2} show the signal of the carbenic carbon at 187.2 ppm (SI).^[5]

Calculations^[15] (SI) demonstrate the extended π-conjugation between the NHC unit and the other fused phenyl rings within the π-helical carbenic ligand along with efficient electronic interaction between the [5]helicene-NHC and the metal center. For example, the HOMO (H) and H-2 of **A**^{1,2} span over Ir and the helicene-NHC-tolyl, while the LUMO (L) and L+2 correspond almost purely to the helicene-NHC π-helical system (Figure 2c, SI). The strong interaction between the π-helical NHC and Ir(III) has been confirmed with ETS-NOCV charge and bonding energy decomposition analyses (SI),^[15b] which revealed a dative NHC-metal bond with NHC→Ir σ-donation and Ir→NHC back-donation, typical for carbenic ligands,^[15c] and with the π-back-bonding clearly enhanced due to the extended π-helicene system. These electronic features may account for the good stability and unprecedented photophysical and (chir)optical properties of **A**^{1,2} (*vide infra*).

Since the methyl group at the N1 position blocks the helical inversion, enantiomerically enriched samples of (*M*,Δ_{Ir})- and (*P*,Δ_{Ir})-**A**¹ and of (*M*,Δ_{Ir})- and (*P*,Δ_{Ir})-**A**² were prepared by HPLC separation over chiral stationary phases (ee's 96-99%, SI).[†] Refluxing of stereoisomerically pure samples in chloroform for several hours did not lead to any epimerization process, showing the high configurational stability of the [5]helicene carbenic ligand (inversion barrier >125 kJ mol⁻¹) and the Ir center. Electronic circular dichroism (ECD) spectra in CH₂Cl₂ are depicted in Figure 2a. Each pair of enantiomers reveal mirror-image spectra, with (*P*,Δ_{Ir})-**A**¹ displaying a set of two positive ECD bands at 252 nm (Δε = +38 M⁻¹ cm⁻¹) and 276 (+43), another set of two positive ECD bands at 312 (+73) and 340 (+58), and a weak negative band at 402 (-14), and (*P*,Δ_{Ir})-**A**² showing bands at 257 nm (Δε = +78 M⁻¹ cm⁻¹), 278 (-38), 302 (-44), 332 (40), and 403 (-13). Interestingly, (*P*,Δ_{Ir})-**A**¹ and (*P*,Δ_{Ir})-**A**² possess ECD bands at similar wavelengths but some with an opposite sign (e.g. at ca. 275 and 305 nm). Furthermore, the

positive intensity around 255 / 335 nm is visibly increased / decreased for (*P*,Δ_{Ir})-**A**² vs. (*P*,Δ_{Ir})-**A**¹. All these features reflect the impact of the pseudo-octahedral iridium stereochemistry. Effects of both Ir and helicene-NHC chirality is further demonstrated by a comparison of the ECD spectra for **A**^{1,2} and for the model NHC complex **A**.^[5c] The sign pattern of bands for Δ_{Ir}-**A** and (*P*,Δ_{Ir})-**A**¹ is mostly similar but **A** reveals significantly decreased ECD intensity (not exceeding 30 M⁻¹ cm⁻¹), evidently due to the lack of the helicene (Figure 2a). Note also that the calculated ECD spectra for the parent *P*-[5]helicene-NHC species are blue-shifted and less intense compared to (*P*,Δ_{Ir})-**A**¹, which confirms the reinforcing impact of the metal and helicene-NHC stereochemistry. See SI for all simulated spectra and molecular orbital analysis. The experimental molar rotations (MRs) also reflect differences between the two epimers (SI). (*P*,Δ_{Ir})-**A**¹ displays a strong positive MR at 436 nm (+16520° cm² dmol⁻¹) while (*P*,Δ_{Ir})-**A**² exhibits a negative MR (-2170), suggesting that the contribution of the Δ_{Ir} center compensates and even surpasses the one from the *P*-[5]helicene-NHC.

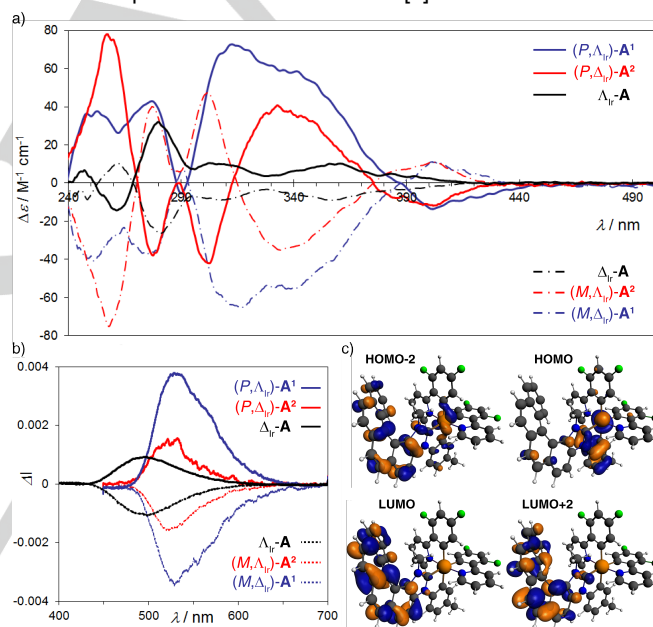


Figure 2. a) ECD spectra of (*P*,Δ_{Ir})-**A**¹ and (*P*,Δ_{Ir})-**A**², of their mirror-images (*M*,Δ_{Ir})-**A**¹ and (*M*,Δ_{Ir})-**A**², and of Δ_{Ir}-**A**. b) CPL spectra of (*M*,Δ_{Ir})-/(*P*,Δ_{Ir})-**A**¹, (*M*,Δ_{Ir})-/(*P*,Δ_{Ir})-**A**² and Δ_{Ir}-**A** at r.t. Each spectrum is normalized to the maximum of its photoluminescence spectrum. c) Isosurfaces (0.04 au) of selected MOs of (*P*,Δ_{Ir})-**A**¹.

The efficient interaction between the π-helical NHC and Ir(III) is also reflected in the emission properties of **A**^{1,2} (SI). Both complexes display vibrationally structured light-green phosphorescence with the 0,0 band maximum at 525 nm and quantum yields of ca. 9-13%. The **A**^{1,2} emission is red-shifted compared to that of the NHC model **A** which displays a blue-green phosphorescence with the 0,0 band at 498 nm. Particularly striking are the phosphorescence lifetimes of ~300 μs observed for **A**^{1,2} which are much longer than values of 1 μs typically recorded for tris-cyclometalated Ir(III) complexes, or the 3.1 μs observed for **A**. *The measured lifetimes are amongst the longest reported for cycloiridiated systems.*^[16,17] As a result, the luminescence of these complexes is extremely sensitive to oxygen. Lifetimes decrease by a factor of greater than 500 upon aeration of the samples in solution at r. t. (Table S2 in SI). The

bimolecular rate constants for quenching by oxygen are of the order of $8.5 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (estimated from the lifetimes under these conditions), which are typical of diffusional quenching for molecular phosphors in solution. Efficient sensitisation of singlet oxygen may be anticipated.^[18] Time-dependent DFT (PBE0/SV(P), CH_2Cl_2 continuum solvent model, SI) calculations^[15a] correctly reproduce changes in the phosphorescence energies for $\mathbf{A}^{1,2}$ vs. \mathbf{A} and link the emission features of $\mathbf{A}^{1,2}$ to the extended π -conjugation in the helical NHC ligand. For \mathbf{A} , the phosphorescence transition is $\text{Ir} \rightarrow \text{dfppy}$ metal-ligand (ML) charge transfer (CT).^[5c] In contrast, the T_1 excited state of $\mathbf{A}^{1,2}$, exhibiting mixed $\text{Ir-NHC-tolyl-helicene, dfppy} \rightarrow \text{NHC-helicene ML} / \text{intraligand} / \text{ligand-ligand}$ CT character, is strongly delocalized across the [5]helicene-NHC, which lowers its energy. Lesser Ir orbital participation (lesser MLCT character) in the T_1 emission for $\mathbf{A}^{1,2}$ vs. \mathbf{A} is consistent with the increase in the emission lifetime for the former and indicates that the spin-orbit coupling at the metal ion in $\mathbf{A}^{1,2}$ is attenuated, yet still sufficient to promote the formally spin-forbidden $T_1 \rightarrow S_0$ process to the extent that it can compete with non-radiative decay.^[16] The result is interesting to compare with platinahelicenes, which reveal relatively long-lived phosphorescence in an even more red-shifted region (620 nm) but with shorter lifetimes (20 μs).^[19]

Circularly polarized luminescence (CPL) spectra of all enantiopure stereoisomers of \mathbf{A} and $\mathbf{A}^{1,2}$ were measured in deoxygenated CH_2Cl_2 samples ($C \sim 10^{-5} \text{ M}$) and are depicted in Figure 2b. Each pair of enantiomers display mirror-image CP phosphorescence with dissymmetry factors^[20] g_{lum} of $+9 \cdot 10^{-4}$ at 493 nm for $(\Delta_{\text{Ir}})\text{-}\mathbf{A}$, and of $+3.7 \cdot 10^{-3}$ and $+1.5 \cdot 10^{-3}$ at 530 nm for respectively $(P, \Delta_{\text{Ir}})\text{-}\mathbf{A}^1$ and $(P, \Delta_{\text{Ir}})\text{-}\mathbf{A}^2$, revealing that the stereochemistry of the π -helical NHC ligand controls the sign of the CPL signal with a value 3 times higher for epimer $(P, \Delta_{\text{Ir}})\text{-}\mathbf{A}^1$ vs. $(P, \Delta_{\text{Ir}})\text{-}\mathbf{A}^2$. Here again, manipulating the Ir(III) stereochemistry enables the CPL to be modified.

In summary, this new diversification in organometallic helicene chemistry provides the molecules with unprecedented features and opens a new field, namely NHCs in helicenes. The Ir-NHC-helicene complexes display very long-lived CP blue-green phosphorescence which may lead to future applications as chiral dopants in CP-OLEDs,^[21a] singlet oxygen sensitizers, or selective photo-oxidizing agents.^[4j, 18, 21b]

Acknowledgements

This work was supported by the ANR (12-BS07-0004-METALHEL-01) and the Chirafun CNRS network. Thibault Reynaldo is thanked for technical support and Dr. Marc Mauduit for fruitful discussions. MS-H acknowledges the young researchers' T-subsidy from the Ministry of Science and Higher Education in Poland. JA acknowledges NSF Grant CHE-1560881 and the Center for Computational Research in Buffalo.

Keywords: helicenes, chiral N-heterocyclic carbenes, cycloiridiated complexes, chiroptical properties, phosphorescence

Notes and references

* Attempts to enantiomerically resolve **5** have failed. Indeed, semi-preparative and analytical separations of helical salts are very rare.

- See: a) D. Koval, L. Severa, L. Adriaenssens, J. Vavra, F. Teply, V. Kasicka, *Electrophoresis* **2011**, 32, 2683; b) G. M. Labrador, J. Bosson, Z. S. Breitbach, Y. Lim, E. R. Francotte, R. Sabia, C. Villani, D. W. Armstrong, J. Lacour, *Chirality* **2016**, 28, 282.
- † The diastereomeric mixture of \mathbf{A}^1 and \mathbf{A}^2 was eluted with hexane / 2-PrOH / chloroform (7/1/2 : v/v/v) on Chiralpak IA to obtain $(M, \Delta_{\text{Ir}})\text{-}\mathbf{A}^1$, $(M, \Delta_{\text{Ir}})\text{-}\mathbf{A}^2$ and the mixture of $(P, \Delta_{\text{Ir}})\text{-}\mathbf{A}^1$ and $(P, \Delta_{\text{Ir}})\text{-}\mathbf{A}^2$, which was subsequently separated on (S,S)-Whelk-O1 column. See SI for details.
- a) H. Amouri, M. Gruselle, *Chirality in Transition Metal Chemistry: Molecules, Supramolecular Assemblies and Materials*, Wiley-VCH, **2009**; b) M. Helms, Z. Lin, L. Gong, K. Harms, E. Meggers, *Eur. J. Inorg. Chem.* **2013**, 4164 and refs therein.
 - a) H. Yersin, (ed.) *Highly Efficient OLEDs with Phosphorescent Materials*, Wiley VCH, **2008**; b) C. Ulbricht, B. Beyer, C. Friebe, A. Winter, U.S. Schubert, *Adv. Mater.* **2009**, 21, 4418.
 - a) J.M. Hearn, I. Romero-Canelon, B. Qamar, Z. Liu, I. Hands-Portman, P.J. Sadler, *ACS Chem. Biol.* **2013**, 8, 1335; b) L. Lu, L.-J. Liu, W.-C. Chao, H.-J. Zhong, M. Wang, X.-P. Chen, J.-J. Lu, R.-N. Li, D.-L. Ma, C.-H. Leung, *Sci. Rep.* **2015**, 5, 14544.
 - a) C. Schaffner-Hamann, A. von Zelewsky, A. Barbieri, F. Barigelletti, G. Muller, J.P. Riehl, A. Neels, *J. Am. Chem. Soc.* **2004**, 126, 9339; b) F.J. Coughlin, M.S. Westrol, K.D. Oyler, N. Byrne, C. Kraml, E. Zysman-Colman, M.S. Lowry, S. Bernhard, *Inorg. Chem.* **2008**, 47, 2039; c) L. Yang, A. von Zelewsky, H. P. Nguyen, G. Muller, G. Labat, H. Stoeckli-Evans, *Inorg. Chim. Acta* **2009**, 362, 3853; d) C.-H. Leung, H.-J. Zhong, H. Yang, Z. Cheng, D.S.H. Chan, V.P.-Y. Ma, R. Abagyan, C.-Y. Wong, D.L. Ma, *Angew. Chem. Int. Ed.* **2012**, 51, 9010; e) E. Marchi, R. Sinisi, G. Bergamini, M. Tragni, M. Monari, M. Bandini, P. Ceroni, *Chem. Eur. J.* **2012**, 18, 8765; f) T.-Y. Li, Y.-M. Jing, X. Liu, Y. Zhao, L. Shi, Z. Tang, Y.-X. Zheng, J. L. Zuo, *Sci. Rep.* **2015**, 5, 14912; g) C. Citti, U. M. Battisti, G. Ciccarella, V. Maiorano, G. Gigli, S. Abbate, G. Mazzeo, E. Castiglioni, G. Longhi, G. Cannazza, *J. Chromatogr. A* **2016**, 1467, 335; h) G. Mazzeo, M. Fusè, G. Longhi, I. Rimoldi, E. Cesarotti, A. Crispini, S. Abbate, *Dalton Trans.* **2016**, 45, 992; i) T.-Y. Li, Y.-X. Zheng, Y.-H. Zhou, *Dalton Trans.* **2016**, 45, 19234; j) L. Zhang, E. Meggers, *Acc. Chem. Res.* **2017**, 50, 320.
 - a) T. Sajoto, P.I. Djurovich, A. Tamayo, M. Yousufuddin, R. Bau, M.E. Thompson, R.J. Holmes, S.R. Forrest, *Inorg. Chem.* **2005**, 44, 7992; b) C.-F. Chang, Y.-M. Cheng, Y. Chi, Y.-C. Chiu, C.-C. Lin, G.-H. Lee, P.-T. Chou, C.-C. Chen, C.-H. Chang, C.-C. Wu, *Angew. Chem. Int. Ed.* **2008**, 47, 4542; c) T.-Y. Li, X. Liang, L. Zhou, C. Wu, S. Zhang, X. Liu, G.-Z. Lu, L.-S. Xue, Y.-X. Zheng, J.-L. Zu, *Inorg. Chem.* **2015**, 54, 161; d) J. Lee, H.-F. Chen, T. Batagoda, C. Coburn, P.I. Djurovich, M.E. Thompson, S.R. Forrest, *Nature Mater.* **2016**, 15, 92; e) P.-H. Lanoë, J. Chan, G. Gontard, F. Monti, N. Armaroli, A. Barbieri, H. Amouri, *Eur. J. Inorg. Chem.* **2016**, 1631.
 - Reviews on applications of NHC metal complexes: a) M. Merics, M. Albrecht, *Chem. Soc. Rev.* **2010**, 39, 1903; b) R. Visbal, M.C. Gimeno, *Chem. Soc. Rev.* **2014**, 43, 3551; c) I. Omae, *Coord. Chem. Rev.* **2016**, 310, 154.
 - Reviews on chiral NHCs: a) V. César, S. Bellemin-Laponnaz, L.H. Gade, *Chem. Soc. Rev.* **2004**, 33, 619; b) F. Wang, L.-J. Liu, W. Wang, S. Li, M. Shi, *Coord. Chem. Rev.* **2012**, 256, 804.
 - Pseudo-helicenic Ir/Rh complexes: W.A. Herrmann, D. Baskakov, E. Herdtweck, S.D. Hoffmann, T. Bunlaksananusorn, F. Rampf, L. Rodefeld, *Organometallics* **2006**, 25, 2449.
 - a) T. Biet, K. Martin, J. Hankache, N. Hellou, A. Hauser, T. Bürgi, N. Vanthuyne, T. Aharon, M. Caricato, J. Crassous, N. Avarvari, *Chem. Eur. J.* **2017**, 23, 437; b) A.J. McConnell, M. Hee Lim, E.D. Olmon, H. Song, E.E. Dervan, J.K. Barton, *Inorg. Chem.* **2012**, 51, 12511; c) Z.-H. Zhang, J.-J. Li, Y.-Z. Gao, Y.-H. Liu, *J. Heterocyclic Chem.* **2007**, 44, 1509.
 - a) C.I. Nieto, P. Cabildo, M. Ángeles García, R.M. Claramunt, I. Alkorta, J. Elguero, *Beilstein J. Org. Chem.* **2014**, 10, 1620; b) A. Escande, J.L. Galigné, *Acta Cryst.* **1974**, B30, 1647.
 - J.X. Qiao, P.Y.S. Lam in *Boronic Acids: Preparation and Applications in Organic Synthesis Medicine and Materials*, 2 ed. (Ed.: D. G. Hall), Wiley-VCH, Weinheim, **2011**, pp. 315-361.
 - K. Yamamoto, M. Okazumi, H. Suemune, K. Usui, *Org. Lett.* **2013**, 15, 1806.

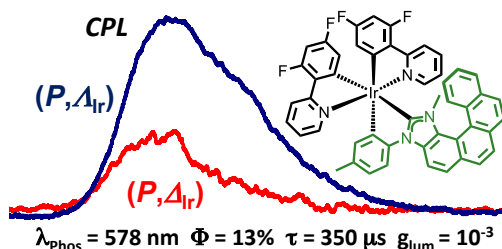
- [13] A.B. Tamayo, B.D. Alleyne, P.I. Djurovich, S. Lamansky, I. Tsyba, N.N. Ho, R. Bau, M.E. Thompson, *J. Am. Chem. Soc.* **2003**, *125*, 7377.
- [14] We recently reported the first cycloiridiated complex bearing a [6]helicene-CH₂-NHC ligand: N. Hellou, C. Jahier-Diallo, O. Baslé, M. Srebro-Hooper, L. Toupet, T. Roisnel, E. Caytan, C. Roussel, N. Vanthuyne, J. Autschbach, M. Mauduit, J. Crassous, *Chem. Comm.* **2016**, *52*, 9243. See also: I. G. Sánchez, M. Šámal, J. Nejedlý, M. Karras, J. Klívar, J. Rybáček, M. Buděšínský, L. Bednárová, B. Seidlerová, I. G. Stará, I. Starý, *Chem. Commun.*, **2017**, *53*, 4370.
- [15] a) J. Autschbach, *Calculating electronic optical activity of coordination compounds*, in K. Poeppelmeier, J. Reedijk, (eds), *Comprehensive Inorganic Chemistry II*, volume 9, Elsevier, Oxford, UK, **2013**, pp. 407-426; b) M. P. Mitoraj, A. Michalak, T. Ziegler, *J. Chem. Theory Comput.* **2009**, *5*, 962; c) M. Srebro, A. Michalak, *Inorg. Chem.* **2009**, *48*, 5361.
- [16] Some Ir complexes with π -extended chromophores and long-lived triplet states are suitable as triplet-triplet annihilation, but not as luminophores. See: J.F. Sun, F.F. Zhong, X.Y. Yi, J.Z. Zhao, *Inorg. Chem.* **2013**, *52*, 6299.
- [17] Non-cyclometalated, N₆-coordinated Ir(III) complexes may display lifetimes of comparable magnitude, where the metal orbitals lie too low in energy to mix effectively with ligand-centred excited states. See: W. Leslie, A.S. Batsanov, J.A.K. Howard, J.A.G. Williams, *Dalton Trans.* **2004**, 623.
- [18] R. Gao, D.G. Ho, B. Hernandez, M. Selke, D. Murphy, P.I. Djurovich, M.E. Thompson, *J. Am. Chem. Soc.* **2002**, *124*, 14828.
- [19] a) L. Norel, M. Rudolph, N. Vanthuyne, J. A. G. Williams, C. Lescop, C. Roussel, J. Autschbach, J. Crassous, R. Réau, *Angew. Chem. Int. Ed.* **2010**, *49*, 9999; b) C. Shen, E. Anger, M. Srebro, N. Vanthuyne, K.K. Deol, T.D. Jefferson Jr., G. Muller, J.A.G. Williams, L. Toupet, C. Roussel, J. Autschbach, R. Réau, J. Crassous, *Chem. Sci.* **2014**, *5*, 1915. Selected other examples of CPL-active helicenes: c) J. E. Field, G. Muller, J. P. Riehl, D. Venkataraman, *J. Am. Chem. Soc.* **2003**, *125*, 11808; d) K. E. S. Phillips, T. J. Katz, S. Jockusch, A. J. Lovinger, N. J. Turro, *J. Am. Chem. Soc.* **2001**, *123*, 11899; e) K. Nakamura, S. Furumi, M. Takeuchi, T. Shibuya, K. Tanaka, *J. Am. Chem. Soc.* **2014**, *136*, 5555; f) N. Saleh, M. Srebro, T. Reynaldo, N. Vanthuyne, L. Toupet, V. Y. Chang, G. Muller, J. A. G. Williams, C. Roussel, J. Autschbach, J. Crassous, *Chem. Comm.* **2015**, *51*, 3754; g) I. Hernandez Delgado, S. Pascal, A. Wallabregue, R. Duwald, C. Besnard, L. Guénée, C. Nançoz, E. Vauthey, R. C. Tovar, J. L. Lunkley, G. Muller, J. Lacour, *Chem. Sci.* **2016**, *7*, 4685; h) T. Katayama, S. Nakatsuka, H. Hirai, N. Yasuda, J. Kumar, T. Kawai, T. Hatakeyama, *J. Am. Chem. Soc.* **2016**, *138*, 5210.
- [20] a) F. Zinna, L. Di Bari, *Chirality* **2015**, *27*, 1; b) E.M. Sanchez-Carnerero, A.R. Agarrabeitia, F. Moreno, B.L. Maroto, G. Muller, M.J. Ortiz, S. de la Moya, *Chem. Eur. J.* **2015**, *21*, 13488.
- [21] a) J.R. Brandt, X. Wang, Y. Yang, A.J. Campbell, M.J. Fuchter, *J. Am. Chem. Soc.* **2016**, *138*, 9743; b) S.C.J. Meskers, H.P.J.M. Dekkers, *Spectrochim. Acta A* **1999**, *55*, 1857.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

The first fused π -helical N-heterocyclic system has been prepared and examined through its enantiomerically and diastereoisomerically pure cycloiridiated complexes. The systems display long-lived circularly polarized phosphorescence, attributed to the extended π -conjugation within the helical carbenic ligand efficiently interacting with the Ir(III) center.



N. Hellou, M. Srebro-Hooper,* L. Favereau, F. Zinna, E. Caytan, L. Toupet, V. Dorcet, M. Jean, N. Vanthuyne, J. A. G. Williams, L. Di Bari, J. Autschbach, and J. Crassous*

Page No. – Page No.

Enantiopure cycloiridiated complexes bearing a pentahelicenic N-heterocyclic carbene and displaying long-lived circularly-polarized phosphorescence